

A17 ~~Flame-resistant polycarbonate/ABS moulding compositions~~

5 The present invention relates to polycarbonate/ABS moulding compositions containing phosphazenes and inorganic nanoparticles, which compositions exhibit excellent flameproofing and very good mechanical properties.

10 DE-A 196 16 968 describes polymerisable phosphazene derivatives, a process for the production thereof and the use thereof as curable binders for lacquers, coatings, fillers, surfacing compositions, adhesives, mouldings or films.

WO 97/40092 describes flameproofed moulding compositions prepared from thermoplastic polymers and unsubstituted phosphazenes of the type $PN_{n-x}H_{1-y}$.

15 EP-A 728 811 describes a thermoplastic blend consisting of aromatic polycarbonate, graft copolymer, copolymer and phosphazenes which exhibits good flameproofing properties, impact strength and heat resistance.

Neither WO 97/400 92 nor EP-A 728 811 describe a combination of phosphazenes and inorganic nanoparticles.

20 The object of the present invention is to provide polycarbonate/ABS moulding compositions having excellent flame resistance, elevated heat resistance and excellent mechanical properties such as notched impact strength, weld line strength and stress cracking resistance. This combination of properties is required in particular for
25 applications in data processing, such as for example casings for monitors, printers or copiers *etc.*.

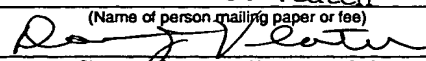
30 It has now been found that PC/ABS moulding compositions which contain phosphazenes in combination with inorganic nanoparticles exhibit the desired properties.

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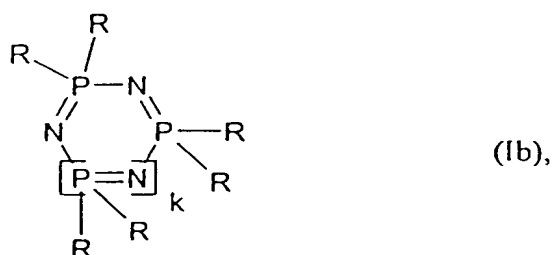
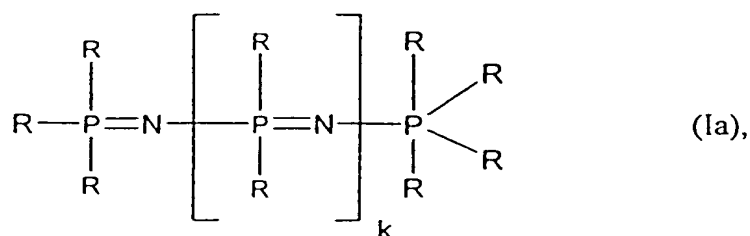
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The present invention accordingly provides thermoplastic moulding compositions containing polycarbonate and/or polyester carbonate, graft polymer, phosphazenes and inorganic powder having an average particle diameter of less than or equal to 200 nm, which compositions may contain further polymers, for example thermoplastic vinyl (co)polymers and/or polyalkylene terephthalates and optionally other additives.

The present invention preferably provides thermoplastic moulding compositions containing

- 10 A) 40 to 99, preferably 60 to 98.5 parts by weight of aromatic polycarbonate and/or polyester carbonate
- B) 0.5 to 60, preferably 1 to 40, in particular 2 to 25 parts by weight of graft polymer of
- 15 B.1) 5 to 95, preferably 30 to 80 wt.% of one or more vinyl monomers on
- B.2) 95 to 5, preferably 20 to 70 wt.% of one or more grafting backbones having a glass transition temperature of $<10^{\circ}\text{C}$, preferably of $<0^{\circ}\text{C}$, particularly preferably of $<-20^{\circ}\text{C}$,
- 20 C) 0 to 45, preferably 0 to 30, particularly preferably 2 to 25 parts by weight of at least one thermoplastic polymer selected from the group comprising vinyl (co)polymers and polyalkylene terephthalates,
- 25 D) 0.1 to 50, preferably 2 to 35, in particular 5 to 25 parts by weight of at least one component selected from the group comprising phosphazenes of the formulae



in which

R is in each case identical or different and denotes amino, C₁ to C₈ alkyl, in each case optionally halogenated, preferably halogenated with fluorine, or C₁ to C₈ alkoxy, C₅ to C₆ cycloalkyl, C₆ to C₂₀ aryl, preferably phenoxy, naphthyloxy, or C₇ to C₁₂ aralkyl, preferably phenyl-C₁-C₄-alkyl, in each case optionally substituted by alkyl, preferably C₁-C₄ alkyl, and/or halogen, preferably chlorine and/or bromine

k denotes 0 or a number from 1 to 15, preferably a number from 1 to 10,

E) 0.5 to 40 parts by weight, preferably 1 to 25, particularly preferably 2 to 15 parts by weight of finely divided inorganic powder having an average particle diameter of less than or equal to 200 nm, and

- F) 0 to 5 parts by weight, preferably 0.15 to 1 part by weight, particularly preferably 0.1 to 0.5 parts by weight of fluorinated polyolefin.

Component A

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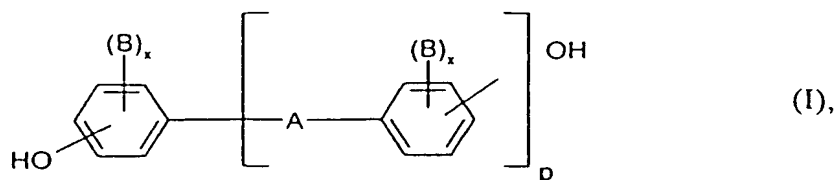
Component A aromatic polycarbonates and/or aromatic polyester carbonates which are suitable according to the invention are known from the literature or may be produced using processes known from the literature (*c.f.* in relation to the production of aromatic polycarbonates, for example Schnell, *Chemistry & Physics of Polycarbonates*, Interscience Publishers, 1964 and DE-AS 1 495 626, DE-OS 2 232 877, DE-OS 2 703 376, DE-OS 2 714 544, DE-OS 3 000 610, DE-OS 3 832 396; in relation to the production of polyester carbonates for example DE-OS 3 077 934).

15 Aromatic polycarbonates are produced for example by reacting diphenols with carbonic acid halides, preferably phosgene, and/or with aromatic dicarboxylic acid dihalides, preferably benzenedicarboxylic acid dihalides, by the phase interface process, optionally using chain terminators, for example monophenols, and optionally using trifunctional or greater than trifunctional branching agents, for example triphenols or tetraphenols.

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Diphenols for the production of the aromatic polycarbonates and/or aromatic polyester carbonates are preferably those of the formula (I)

25



30

wherein

5 or a residue of the formula (II) or (III)



20 x in each case mutually independently mean 0, 1 or 2,

25 R⁵ and R⁶ mutually independently, individually selectably for each X¹, mean hydrogen or C₁-C₆ alkyl, preferably hydrogen, methyl or ethyl,

m means an integer from 4 to 7, preferably 4 or 5, providing that R⁵ and R⁶ are simultaneously alkyl on at least one atom X¹.

Preferred diphenols are hydroquinone, resorcinol, dihydroxydiphenols, bis-(hydroxyphenyl)-C₁-C₅-alkanes, bis-(hydroxyphenyl)-C₅-C₆-cycloalkanes, bis-(hydroxyphenyl) ethers, bis-(hydroxyphenyl) sulfoxides, bis-(hydroxyphenyl) ketones, bis-(hydroxyphenyl) sulfones and α,α -bis-(hydroxyphenyl)diisopropylbenzenes together with the ring-brominated and/or ring-chlorinated derivatives thereof.

Particularly preferred diphenols are 4,4'-dihydroxydiphenyl, bisphenol A, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)cyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl sulfone together with the di- and tetrabrominated or chlorinated derivatives thereof, such as for example 2,2-bis-(3-chloro-4-hydroxyphenyl)propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)propane or 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)propane.

2,2-Bis-(4-hydroxyphenyl)propane (bisphenol A) is particularly preferred.

The diphenols may be used individually or as any desired mixtures.

The diphenols are known from the literature or are obtainable using processes known from the literature.

Chain terminators suitable for the production of the thermoplastic, aromatic polycarbonates are, for example, phenol, p-chlorophenol, p-tert.-butylphenol or 2,4,6-tribromophenol, as well as long-chain alkylphenols, such as 4-(1,3-tetramethylbutyl)phenol according to DE-OS 2 842 005 or monoalkylphenol or dialkylphenols having a total of 8 to 20 C atoms in the alkyl substituents, such as 3,5-di-tert.-butylphenol, p-iso-octylphenol, p-tert.-octylphenol, p-dodecylphenol and 2-(3,5-dimethylheptyl)phenol and 4-(3,5-dimethylheptyl)phenol. The quantity of chain terminators to be used is generally between 0.5 mol% and 10 mol%, relative to the sum of moles of the diphenols used in each case.

The thermoplastic, aromatic polycarbonates have weight average molecular weights (M_w , measured for example by ultracentrifugation or light scattering) of 10000 to 200000, preferably of 20000 to 80000.

5 The thermoplastic, aromatic polycarbonates may be branched in a known manner, preferably by incorporating 0.05 to 2.0 mol%, relative to the sum of diphenols used, of trifunctional or greater than trifunctional compounds, for example those having three and more than three phenolic groups.

10 Both homopolycarbonates and copolycarbonates are suitable. Component A copolycarbonates according to the invention may be produced by also using 1 to 25 wt.%, preferably 2.5 to 25 wt.% (relative to the total quantity of diphenols to be used) of polydiorganosiloxanes having hydroxy-aryloxy end groups. These are known (*c.f.* for example US patent 3 419 634) or may be produced using processes known
15 from the literature. The production of copolycarbonates containing polydiorganosiloxanes is described, for example, in DE-OS 3 334 782.

Preferred polycarbonates, apart from bisphenol A homopolycarbonates, are copolycarbonates of bisphenol A with up to 15 mol%, relative to the sum of moles of
20 diphenols, of other diphenols mentioned as preferred or particularly preferred, in particular 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)propane.

Aromatic dicarboxylic acid dihalides for the production of aromatic polyester carbonates are preferably the diacid dichlorides of isophthalic acid, terephthalic acid,
25 diphenyl ether 4,4'-dicarboxylic acid and 2,6-naphthalenedicarboxylic acid.

Mixtures of the diacid dichlorides of isophthalic acid and terephthalic acid in a ratio of between 1:20 and 20:1 are particularly preferred.

30 A carbonic acid halide, preferably phosgene, is additionally used as a difunctional acid derivative in the production of polyester carbonates.

Chain terminators which may be considered for the production of the aromatic polyester carbonates are, apart from the above-mentioned monophenols, also the chlorocarbonic acid esters thereof and the acid chlorides of aromatic monocarboxylic acids, which may optionally be substituted by C_1 - C_{22} alkyl groups or by halogen atoms, together with aliphatic C_2 - C_{22} monocarboxylic acid chlorides.

The quantity of chain terminators is in each case 0.1 to 10 mol%, relative, in the case of phenolic chain terminators, to the number of moles of diphenols and, in the case of monocarboxylic acid chloride chain terminators, to the number of moles of dicarboxylic acid dichlorides.

The aromatic polyester carbonates may also contain incorporated aromatic hydroxycarboxylic acids.

The aromatic polyester carbonates may be both linear and branched in a known manner (*c.f.* in this connection also DE-OS 2 940 024 and DE-OS 3 007 934).

Branching agents which may be used are, for example, tri- or polyfunctional carboxylic acid chlorides, such as trimesic acid trichloride, cyanuric acid trichloride, 3,3',4,4'-benzophenonetetracarboxylic acid tetrachloride, 1,4,5,8-naphthalene-tetracarboxylic acid tetrachloride or pyromellitic acid tetrachloride, in quantities of 0.01 to 1.0 mol% (relative to dicarboxylic acid dichlorides used) or tri- or polyfunctional phenols, such as phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-2-heptene, 4,4-dimethyl-2,4,6-tri-(4-hydroxyphenyl)heptane, 1,3,5-tri-(4-hydroxyphenyl)benzene, 1,1,1-tri-(4-hydroxyphenyl)ethane, tri-(4-hydroxyphenyl)-phenylmethane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)cyclohexyl]propane, 2,4-bis-(4-hydroxyphenylisopropyl)phenol, tetra-(4-hydroxyphenyl)methane, 2,6-bis-(2-hydroxy-5-methylbenzyl)-4-methylphenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)propane, tetra-(4-[4-hydroxyphenylisopropyl]phenoxy)methane, 1,4-bis[4,4'-dihydroxytriphenyl)methyl]benzene, in quantities of 0.01 to 1.0 mol%,

relative to diphenols used. Phenolic branching agents may be introduced initially with the diphenols, acid chloride branching agents may be introduced together with the acid dichlorides.

- 5 The proportion of carbonate structural units in the thermoplastic, aromatic polyester carbonates may be varied at will. The proportion of carbonate groups is preferably up to 100 mol%, in particular up to 80 mol%, particularly preferably up to 50 mol%, relative to the sum of ester groups and carbonate groups. Both the ester and carbonate fractions of the aromatic polyester carbonates may be present in the form of blocks or
- 10 randomly distributed in the polycondensation product.

- The relative solution viscosity (η_{rel}) of the aromatic polycarbonates and polyester carbonates is in the range from 1.18 to 1.4, preferably from 1.22 to 1.3 (measured on solutions of 0.5 g of polyester carbonate in 100 ml of methylene chloride solution at
- 15 25°C).

The thermoplastic, aromatic polycarbonates and polyester carbonates may be used alone or as any desired mixture with each other.

20 **Component B**

Component B comprises one or more graft polymers of

- B.1 5 to 95, preferably 30 to 80 wt.%, of at least one vinyl monomer on
- 25 B.2 95 to 5, preferably 70 to 20 wt.%, of one or more graft backbones having glass transition temperatures of $<10^{\circ}\text{C}$, preferably of $<0^{\circ}\text{C}$, particularly preferably of $<-20^{\circ}\text{C}$.

The grafting backbone B.2 generally has an average particle size (d_{50} value) of 0.05 to 5 μm , preferably of 0.10 to 0.5 μm , particularly preferably of 0.20 to 0.40 μm .

5 Monomers B.1 are preferably mixtures of

10 B.1.1 50 to 99 parts by weight of vinyl aromatics and/or ring-substituted vinyl aromatics (such as for example styrene, α -methylstyrene, p-methylstyrene, p-chlorostyrene) and/or methacrylic acid ($\text{C}_1\text{-C}_4$)-alkyl esters (such as for example methyl methacrylate, ethyl methacrylate) and

15 B.1.2 1 to 50 parts by weight of vinyl cyanides (unsaturated nitriles such as acrylonitrile and methacrylonitrile) and/or (meth)acrylic acid ($\text{C}_1\text{-C}_8$)-alkyl esters (such as for example methyl methacrylate, n-butyl acrylate, t-butyl acrylate) and/or derivatives (such as anhydrides and imides) of unsaturated carboxylic acids (for example maleic anhydride and N-phenylmaleimide).

20 Preferred monomers B.1.1 are selected from among at least one of the monomers styrene, α -methylstyrene and methyl methacrylate, preferred monomers B.1.2 are selected from among at least one of the monomers acrylonitrile, maleic anhydride and methyl methacrylate.

Particularly preferred monomers are B.1.1 styrene and B.1.2 acrylonitrile.

25 Grafting backbones B.2 suitable for the graft polymers B are for example diene rubbers, EP(D)M rubbers, *i.e.* those based on ethylene/propylene and optionally diene, acrylate, polyurethane, silicone, chloroprene and ethylene/vinyl acetate rubbers.

30 Preferred grafting backbones B.2 are diene rubbers (for example based on butadiene, isoprene *etc.*) or mixtures of diene rubbers or copolymers of diene rubbers or mixtures

thereof with further copolymerisable monomers (for example according to B.1.1 and B.1.2), providing that the glass transition temperature of component B.2 is $<10^{\circ}\text{C}$, preferably $<0^{\circ}\text{C}$, particularly preferably $<-10^{\circ}\text{C}$.

5 Pure polybutadiene rubber is particularly preferred.

Particularly preferred polymers B are, for example, ABS polymers (emulsion, bulk and suspension ABS), as are described for example in DE-OS 2 035 390 (= US-PS 3 644 574) or in DE-OS 2 248 242 (= GB-PS 1 409 275) or in Ullmann,
10 *Enzyklopädie der Technischen Chemie*, volume 19 (1980), pp. 280 *et seq.*. The gel content of the grafting backbone B.2 is at least 30 wt.%, preferably at least 40 wt.% (measured in toluene).

The graft copolymers B are produced by free-radical polymerisation, for example by
15 emulsion, suspension, solution or bulk polymerisation, preferably by emulsion polymerisation.

Particularly suitable graft rubbers are ABS polymers which are produced by redox initiation using an initiator system comprising organic hydroperoxide and ascorbic
20 acid according to US-P 4 937 285.

Since, as is known, the graft monomers are not necessarily grafted in their entirety onto the grafting backbone during the grafting reaction, graft polymers B are also taken according to the invention to include those products which are obtained by
25 (co)polymerisation of the graft monomers in the presence of the grafting backbone and are also isolated during working up.

Suitable polymer B acrylate rubbers B.2 are preferably polymers prepared from acrylic acid alkyl esters, optionally with up to 40 wt.%, relative to B.2, of other
30 polymerisable, ethylenically unsaturated monomers. Preferred polymerisable acrylic acid esters include $\text{C}_1\text{-C}_8$ alkyl esters, for example methyl, ethyl, butyl, n-octyl and

2-ethylhexyl esters; haloalkyl esters, preferably halo-C₁-C₈-alkyl esters, such as chloroethyl acrylate and mixtures of these monomers.

Monomers having more than one polymerisable double bond may also be
5 copolymerised for crosslinking purposes. Preferred examples of crosslinking monomers are esters of unsaturated monocarboxylic acids having 3 to 8 C atoms and unsaturated monohydric alcohols having 3 to 12 C atoms, or saturated polyols having 2 to 4 OH groups and 2 to 20 C atoms, such as for example ethylene glycol dimethacrylate, allyl methacrylate; polyunsaturated heterocyclic compounds, such as
10 for example trivinyl and triallyl cyanurate; polyfunctional vinyl compounds, such as di- and trivinylbenzenes; as well as triallyl phosphate and diallyl phthalate.

Preferred crosslinking monomers are allyl methacrylate, ethylene glycol dimethacrylate, diallyl phthalate and heterocyclic compounds having at least three
15 ethylenically unsaturated groups.

Particularly preferred crosslinking monomers are the cyclic monomers triallyl cyanurate, triallyl isocyanurate, triacryloylhexahydro-s-triazine, triallylbenzenes. The quantity of crosslinking monomers is preferably 0.02 to 5, preferably 0.05 to 2 wt.%,
20 relative to the grafting backbone B.2.

It is advantageous to limit the quantity of cyclic crosslinking monomers having at least three ethylenically unsaturated groups to below 1 wt.% of the grafting backbone B.2.

25 Preferred "other" polymerisable, ethylenically unsaturated monomers which, in addition to the acrylic acid esters, may optionally be used to produce the grafting backbone B.2 are, for example, acrylonitrile, styrene, α -methylstyrene, acrylamides, vinyl C₁-C₆-alkyl ethers, methyl methacrylate, butadiene. Preferred acrylate rubbers as
30 the grafting backbone B.2 are emulsion polymers having a gel content of at least 60 wt.%.

Further suitable grafting backbones B.2 are silicone rubbers having active grafting sites, as are described in DE-OS 3 704 657, DE-OS 3 704 655, DE-OS 3 631 540 and DE-OS 3 631 539.

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The gel content of the grafting backbone B.2 is determined in a suitable solvent at 25°C (M. Hoffmann, H. Krömer, R. Kuhn, *Polymeranalytik I & II*, Georg Thieme Verlag, Stuttgart 1977).

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The average particle size d_{50} is the diameter both above and below which 50 wt.% of the particles lie. This value may be measured by ultracentrifugation (W. Scholtan, H. Lange, *Kolloid Z. und Z. Polymere*, 250 (1972), 782-1796).

Component C

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Component C comprises one or more thermoplastic vinyl (co)polymers C.1. and/or polyalkylene terephthalates C.2.

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Suitable vinyl (co)polymers C.1 are polymers of at least one monomer from the group of vinyl aromatics, vinyl cyanides (unsaturated nitriles), (meth)acrylic acid (C_1-C_8)-alkyl esters, unsaturated carboxylic acids and derivatives (such as anhydrides and imides) of unsaturated carboxylic acids. Particularly suitable (co)polymers are those prepared from

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C.1.1 50 to 99, preferably 60 to 80 parts by weight of vinyl aromatics and/or ring-substituted vinyl aromatics such as for example styrene, α -methylstyrene, p-methylstyrene, p-chlorostyrene) and/or methacrylic acid (C_1-C_8)-alkyl esters such as for example methyl methacrylate, ethyl methacrylate) and

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C.1.2 1 to 50, preferably 20 to 40 parts by weight of vinyl cyanides (unsaturated nitriles) such as acrylonitrile and methacrylonitrile and/or (meth)acrylic acid

(C₁-C₈)-alkyl esters (such as for example methyl methacrylate, n-butyl acrylate, t-butyl acrylate) and/or unsaturated carboxylic acids (such as maleic acid) and/or derivatives (such as anhydrides and imides) of unsaturated carboxylic acids (for example maleic anhydride and N-phenylmaleimide).

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The (co)polymers C.1 are resinous, thermoplastic and rubber-free.

The copolymer of C.1.1 styrene and C.1.2 acrylonitrile is particularly preferred.

10 The (co)polymers C.1 are known and may be produced by free-radical polymerisation, in particular by emulsion, suspension, solution or bulk polymerisation. The (co)polymers preferably have molecular weights M_w (weight average, determined by light scattering or sedimentation) of between 15000 and 200000.

15 The component C.2 polyalkylene terephthalates are reaction products of aromatic dicarboxylic acids or the reactive derivatives thereof, such as dimethyl esters or anhydrides, and aliphatic, cycloaliphatic or araliphatic diols, together with mixtures of these reaction products.

20 Preferred polyalkylene terephthalates contain at least 80 wt.%, preferably at least 90 wt.%, relative to the dicarboxylic acid component, of terephthalic acid residues and at least 80 wt.%, preferably at least 90 mol%, relative to the diol component, of ethylene glycol and/or 1,4-butanediol residues.

25 In addition to terephthalic acid residues, the preferred polyalkylene terephthalates may contain up to 20 mol%, preferably up to 10 mol%, of residues of other aromatic or cycloaliphatic dicarboxylic acids having 8 to 14 C atoms or aliphatic dicarboxylic acids having 4 to 12 C atoms, such as for example residues of phthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid,
30 succinic acid, adipic acid, sebacic acid, azelaic acid, cyclohexanediacetic acid.

In addition to ethylene glycol or 1,4-butanediol residues, the preferred polyalkylene terephthalates may contain up to 20 mol%, preferably up to 10 mol%, of other aliphatic diols having 3 to 12 C atoms or cycloaliphatic diols having 6 to 21 C atoms, for example residues of 1,3-propanediol, 2-ethyl-1,3-propanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, 3-ethyl-2,4-pentanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,5-hexanediol, 1,4-di-(β -hydroxyethoxy)benzene, 2,2-bis-(4-hydroxycyclohexyl)propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(4- β -hydroxyethoxyphenyl)propane and 2,2-bis-(4-hydroxypropoxyphenyl)propane (DE-OS 2 407 674, 2 407 776, 2 715 932).

The polyalkylene terephthalates may be branched by incorporating relatively small quantities of tri- or tetrahydric alcohols or tri- or tetrabasic carboxylic acids, for example according to DE-OS 1 900 270 and US-PS 3 692 744. Further preferred branching agents are trimesic acid, trimellitic acid, trimethylolethane and trimethylolpropane and pentaerythritol.

Particularly preferred polyalkylene terephthalates are those solely produced from terephthalic acid and the reactive derivatives thereof (for example the dialkyl esters thereof) and ethylene glycol and/or 1,4-butanediol, and mixtures of these polyalkylene terephthalates.

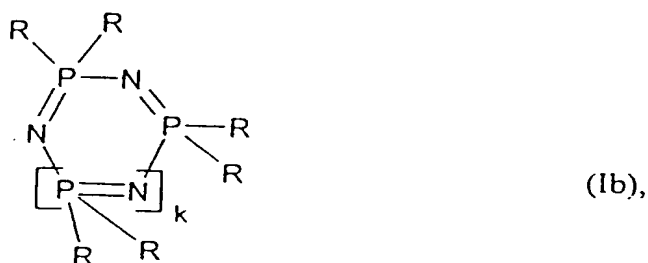
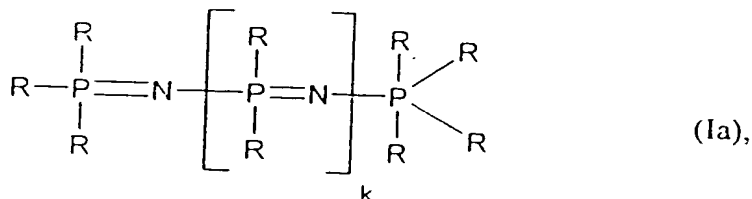
Mixtures of polyalkylene terephthalates contain 1 to 50 wt.%, preferably 1 to 30 wt.%, of polyethylene terephthalate and 50 to 99 wt.%, preferably 70 to 99 wt.%, of polybutylene terephthalate.

The preferably used polyalkylene terephthalates generally have an intrinsic viscosity of 0.4 to 1.5 dl/g, preferably of 0.5 to 1.2 dl/g, measured in phenol/o-dichlorobenzene (1:1 parts by weight) at 25°C in a Ubbelohde viscosimeter.

The polyalkylene terephthalates may be produced using known methods (*c.f.* for example *Kunststoff-Handbuch*, volume VIII, pp. 695 *et seq.*, Carl Hanser Verlag, Munich 1973).

5 Component D

Component D) phosphazenes which are used according to the present invention are linear phosphazenes of the formula (Ia) and cyclic phosphazenes of the formula (Ib)



wherein k and R have the above-stated meaning.

The following may be mentioned by way of example:

25 propoxyphosphazene, phenoxyphosphazene, methylphenoxyphosphazene, amino-phosphazene and fluoroalkylphosphazenes.

Phenoxyphosphazene is preferred.

30 The phosphazenes may be used alone or as a mixture. The residue R may always be identical or two or more residues in the formula (Ia) and (Ib) may be different.

The phosphazenes and the production thereof are described, for example, in EP-A 728 811, DE-A 1 961 668 and WO 97/40092.

5 **Component E**

Component E comprises ultrafinely divided inorganic powders.

10 Ultrafinely divided inorganic powders E used according to the invention preferably consist of at least one polar compound of one or more metals of main groups 1 to 5 or subgroups 1 to 8 of the periodic system, preferably of main groups 2 to 5 or subgroups 4 to 8, particularly preferably of main groups 3 to 5 or subgroups 4 to 8 with at least one element selected from among oxygen, hydrogen, sulfur, phosphorus, boron, carbon, nitrogen or silicon.

15 Preferred compounds are for example oxides, hydroxides, hydrous oxides, sulfates, sulfites, sulfides, carbonates, carbides, nitrates, nitrites, nitrides, borates, silicates, phosphates, hydrides, phosphites or phosphonates.

20 The ultrafinely divided inorganic powders preferably consist of oxides, phosphates, hydroxides, preferably of TiO_2 , SiO_2 , SnO_2 , ZnO , ZnS , boehmite, ZrO_2 , Al_2O_3 , aluminium phosphates, iron oxides, as well as TiN , WC , $\text{AlO}(\text{OH})$, Sb_2O_3 , iron oxides, NaSO_4 , vanadium oxides, zinc borate, silicates such as Al silicates, Mg silicates, 1-, 2- or 3-dimensional silicates. Mixtures and doped compounds may also
25 be used.

These nanoscalar particles may furthermore be surface-modified with organic molecules in order to achieve better compatibility with the polymers. Hydrophobic or hydrophilic surfaces may be produced in this manner.

30 Hydrated aluminium oxides, for example boehmite, or TiO_2 are particularly preferred.

The average particle diameters of the nanoparticles are less than or equal to 200 nm, preferably less than or equal to 150 nm, in particular from 1 to 100 nm.

- 5 Particle size and particle diameter always mean the average particle diameter d_{50} measured by ultracentrifugation in accordance with W. Scholtan *et al.*, *Kolloid-Z. und Z. Polymere* 250 (1972), pp. 782-796.

- 10 The inorganic powder is incorporated into the thermoplastic moulding composition in quantities of 0.5 to 40, preferably of 1 to 25, particularly preferably of 2 to 15 wt.%, relative to the thermoplastic material.

- 15 The inorganic compounds may assume the form of powders, pastes, sols, dispersions or suspensions. Powders may be obtained from dispersions, sols or suspensions by precipitation.

- 20 The powders may be incorporated into the thermoplastic moulding compositions using conventional methods, for example by direct kneading or extrusion of moulding compositions and the ultrafinely divided inorganic powders. Preferred methods include producing a masterbatch, for example in flame retardant additives and at least one component of the moulding compositions according to the invention in monomers or solvents, or coprecipitation of a thermoplastic component and the ultrafinely divided inorganic powders, for example by coprecipitation of an aqueous emulsion and the ultrafinely divided inorganic powders, optionally in the form of dispersions, suspensions, pastes or sols of the ultrafinely divided inorganic materials.
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Component F

- 30 The fluorinated polyolefins F are of a high molecular weight and have glass transition temperatures of above -30°C , generally of above 100°C , fluorine contents preferably of 65 to 76, in particular of 70 to 76 wt.%, average particle diameters d_{50} of 0.05 to

1000, preferably of 0.08 to 20 μm . The fluorinated polyolefins F preferably have a density of 1.2 to 2.3 g/cm^3 . Preferred fluorinated polyolefins F are polytetrafluoroethylene, polyvinylidene fluoride, tetrafluoroethylene/hexafluoropropylene and ethylene/tetrafluoroethylene copolymers. The fluorinated polyolefins are known (*c.f.* 5 *Vinyl & Related Polymers* by Schildknecht, John Wiley & Sons Inc., New York, 1962, pp. 484-494; *Fluoropolymers* by Wall, Wiley-Interscience, John Wiley & Sons Inc., New York, volume 13, 1970, pp. 623-654; *Modern Plastics Encyclopedia*, 1970-1971, volume 47, no. 10 A, October 1970, McGraw-Hill Inc., New York, pp. 134 and 774; *Modern Plastics Encyclopedia*, 1975-1976, October 1975, volume 52, no. 10A, 10 McGraw-Hill Inc., New York, pp. 27, 28 and 472 and US-PS 3 671 487, 3 723 373 and 3 838 092).

They may be produced using known processes, thus for example by polymerising tetrafluoroethylene in an aqueous medium with a free-radical forming catalyst, for 15 example sodium, potassium or ammonium peroxydisulfate, at pressures of 7 to 71 kg/cm^2 and at temperatures of 0 to 200°C, preferably at temperatures of 20 to 100°C. (*c.f.* for example US patent 2 393 967 for further details). Depending upon the form in which they are used, the density of these materials may be between 1.2 and 2.3 g/cm^3 , the average particle size between 0.5 and 1000 μm .

20 Polyolefins F preferred according to the invention are tetrafluoroethylene polymers having average particle diameters of 0.05 to 20 μm , preferably of 0.08 to 10 μm , and a density of 1.2 to 1.9 g/cm^3 and are preferably used in the form of a coagulated mixture of emulsions of tetrafluoroethylene polymers F with emulsions of the graft polymers 25 B.

Suitable polyolefins F usable in powder form are tetrafluoroethylene polymers having average particle diameters of 100 to 1000 μm and densities of 2.0 g/cm^3 to 2.3 g/cm^3 .

A coagulated mixture of B and F is produced by firstly mixing an aqueous emulsion (latex) of a graft polymer B with a finely divided emulsion of a tetraethylene polymer F; suitable tetrafluoroethylene polymer emulsions conventionally have solids contents of 30 to 70 wt.%, in particular of 50 to 60 wt.%, preferably of 30 to 35 wt.%.

5

The quantity stated in the description of component B may include the proportion of the graft polymer for the coagulated mixture prepared from the graft polymer and fluorinated polyolefin.

- 10 The weight ratio of graft polymer B to tetrafluoroethylene polymer F in the emulsion mixture is 95:5 to 60:40. The emulsion mixture is then coagulated in a known manner, for example by spray drying, freeze drying or coagulation by addition of inorganic or organic salts, acids, bases or organic, water-miscible solvents, such as alcohols, ketones, preferably at temperatures of 20 to 150°C, in particular of 50 to 100°C. If
15 necessary, drying may be performed at 50 to 200°C, preferably at 70 to 100°C.

Suitable tetrafluoroethylene polymer emulsions are conventional commercial products and are offered for sale, for example, by DuPont as Teflon® 30 N.

- 20 The moulding compositions according to the invention may contain at least one of the conventional additives, such as lubricants and mould release agents, nucleating agents, antistatic agents, stabilisers as well as dyes and pigments.

- The moulding compositions according to the invention may contain up to 35 wt.%,
25 relative to the overall moulding composition, of a further, optionally synergistic flame retardant. Examples of further flame retardants which may be mentioned are organic phosphorus compounds such as for example described in EP-A 363 608, EP-A 345 522 and EP-A 640 655, organic halogen compounds, such as decabromobisphenyl-ether, tetrabromobisphenol, inorganic halogen compounds such
30 as ammonium bromide, nitrogen compounds, such as melamine,

melamine/formaldehyde resins, inorganic hydroxide compounds, such as Mg, Al hydroxide, inorganic compounds such as antimony oxides, barium metaborate, hydroxoantimonate, zirconium oxide, zirconium hydroxide, molybdenum oxide, ammonium molybdate, zinc borate, ammonium borate, barium metaborate, talc, silicate, silicon dioxide and tin oxide, as well as siloxane compounds.

The moulding compositions according to the invention containing components A to F and optionally further known additives such as stabilisers, dyes, pigments, lubricants and mould release agents, nucleating agents, as well as antistatic agents, are produced by mixing the particular constituents in a known manner and melt-compounding and melt-extruding them at temperatures of 200°C to 300°C in conventional units such as internal kneaders, extruders and twin-screw extruders, wherein component F is preferably used in the form of the above-mentioned coagulated mixture.

The individual constituents may be mixed in a known manner both in succession and simultaneously and both at approx. 20°C (room temperature) and at a higher temperature.

By virtue of their excellent flame resistance and heat resistance together with good properties such as weld line strength and ESC behaviour (stress cracking resistance), the thermoplastic moulding compositions according to the invention are suitable for the production of mouldings of all kinds, in particular those requiring elevated resistance to breakage.

The moulding compositions of the present invention may be used for the production of mouldings of any kind. Mouldings may in particular be produced by injection moulding. Examples of mouldings which may be produced are: casings of all kinds, for example for domestic appliances such as juice extractors, coffee machines, food mixers, for office equipment, such as monitors, printers, copiers or cladding sheet for the building sector and automotive components. They may also be used in electrical engineering applications as they have very good electrical properties.

The moulding compositions according to the invention may furthermore, for example, be used to produce the following mouldings or shaped articles:

5 Interior trim for rail vehicles, hub-caps, casings for electrical devices containing small transformers, casings for information dissemination and transmission devices, casings and cladding for medical purposes, massage devices and casings therefor, toy vehicles for children, sheet wall elements, casings for safety equipment, hatchback spoilers, thermally insulated transport containers, apparatus for keeping or caring for small animals, mouldings for sanitary and bathroom installations, cover grilles for
10 ventilation openings, mouldings for summer houses and sheds, casings for garden appliances.

Another processing method is the production of mouldings by thermoforming of previously produced sheet or film.

15

The present invention accordingly also provides the use of the moulding compositions according to the invention for the production of mouldings of all kinds, preferably those stated above, and the mouldings made from the moulding compositions according to the invention.

Examples

Component A

- 5 Linear bisphenol A based polycarbonate having a relative solution viscosity of 1.252, measured in CH_2Cl_2 as solvent at 25°C and a concentration of 0.5 g/100 ml.

Component B

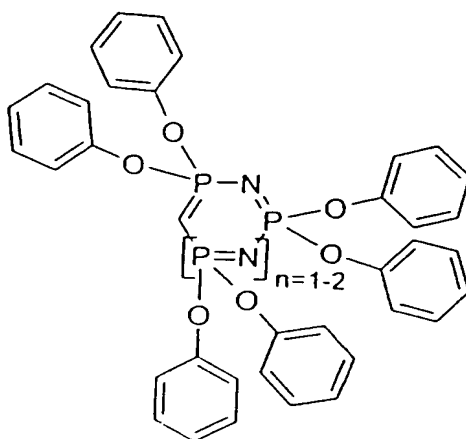
- 10 Graft polymer of 40 parts by weight of a copolymer prepared from styrene and acrylonitrile in a 73:27 ratio on 60 parts by weight of particulate, crosslinked polybutadiene rubber (average particle diameter $d_{50} = 0.28 \mu\text{m}$), produced by emulsion polymerisation.

15 **Component C**

Styrene/acrylonitrile copolymer having a styrene/acrylonitrile weight ratio of 72:28 and an intrinsic viscosity of 0.55 dl/g (measured in dimethylformamide at 20°C).

20 **Component D**

Phenoxyphosphazene of the formula



Commercial product P-3800 from Nippon Soda Co. Ltd., Japan.

Component E

Pural® 200, an aluminium hydroxide (from Condea, Hamburg, Germany), average particle size approx. 50 nm.

Component F

Tetrafluoroethylene polymer as a coagulated mixture prepared from an SAN graft polymer emulsion corresponding to the above-stated component B in water and a tetrafluoroethylene polymer emulsion in water. The weight ratio of graft polymer B to the tetrafluoroethylene polymer F in the mixture is 90 wt.% : 10 wt.%. The tetrafluoroethylene polymer emulsion has a solids content of 60 wt.%, the average particle diameter is between 0.05 and 0.5 μm . The SAN graft polymer emulsion has a solids content of 34 wt.% and an average latex particle diameter of $d_{50} = 0.28 \mu\text{m}$.

Production of F

The emulsion of the tetrafluoroethylene polymer (Teflon 30 N from DuPont) is mixed with the emulsion of the SAN graft polymer B and stabilised with 1.8 wt.%, relative to polymer solids, of phenolic antioxidants. At 85 to 95°C, the mixture is coagulated at pH 4 to 5 with an aqueous solution of MgSO_4 (Epsom salts) and acetic acid, filtered and washed until virtually free of electrolytes, then the principal quantity of water is removed by centrifugation and the material then dried at 100°C to yield a powder. This powder may be compounded with the other components in the units described.

Production and testing of the moulding compositions according to the invention

The components are mixed in a 3 litre internal kneader. The mouldings are produced at 260°C on an Arburg model 270 E injection moulding machine.

The Vicat B softening point is determined to DIN 53 460 (ISO 306) on bars of dimensions $80 \times 10 \times 4$ mm.

Notched impact strength a_k is determined to ISO 180/1 A.

Weld line strength is determined by measuring the impact strength to DIN 53 453 at the weld line of test specimens injection moulded from both sides (processing temperature 260°C) of dimensions $170 \times 10 \times 4$ mm.

The fire behaviour of the specimens was measured to UL-Subj. 94 V on bars of dimensions $127 \times 12.7 \times 1.6$ mm, produced on an injection moulding machine at 260°C.

The UL 94 V test is performed as follows:

- Samples of the material are shaped into bars of dimensions $127 \times 12.7 \times 1.6$ mm. The bars are mounted vertically in such a manner that the underside of the test specimen is in each case 305 mm above a strip of dressing material. Each test bar is individually ignited by means of two successive ignition operations of a duration of 10 s, the burning characteristics after each ignition operation are observed and the specimen then evaluated. The specimen is ignited with a Bunsen burner with a 100 mm (3.8 inch) tall blue flame of natural gas having a calorific content of 3.73×10^4 kJ/m³ (1000 BTU per cubic foot).
- The UL 94 V-0 classification includes the properties described below of materials which have been tested in accordance with the UL 94 V method. The moulding compositions of this class include no samples which burn for longer than 10 s after each exposure to the test flame; they exhibit no total burning times of greater than 50 s on both exposures to flame for each sample set; they include no samples which burn away completely up to the clamp attached at the top of the sample; they include no samples which ignite the cotton wool arranged beneath the sample by burning droplets or particles; they also include no samples which glow for longer than 30 s after removal of the test flame.
- Other UL 94 classifications denote samples which are less flame resistant or less self-extinguishing because they release burning droplets or particles. These classifications are designated UL 94 V-1 and V-2. "Fail" is the classification of samples which have a burning time of ≥ 30 s.
- Stress cracking behaviour (ESC behaviour) was investigated on bars of dimensions $80 \times 10 \times 4$ mm, processing temperature 260°C. The test medium used was a mixture of 60 vol.% toluene and 40 vol.% isopropanol. The test pieces were pre-stressed on a circular arc template (initial elongation in percent) and immersed in the test medium at room temperature. Stress cracking behaviour was evaluated on the basis of cracking or failure as a function of initial elongation in the test medium.

Table 1 below summarises the properties of the moulding compositions according to the invention:

- 5 By using the combination of phosphazene and ultrafinely divided inorganic powder, moulding compositions are obtained having elevated heat resistance, which are distinguished by very good mechanical properties such as notched impact strength, stress cracking resistance and weld line strength. The good flame resistance of the moulding compositions according to the invention is surprisingly achieved with
- 10 distinctly reduced quantities of phosphazene.

Table: Moulding compositions and properties thereof

| | 1 (Comp.) | 2 | 3 |
|--|-----------|------|------|
| Components [parts by weight] | | | |
| A | 66.7 | 66.7 | 66.7 |
| B | 7.3 | 7.3 | 7.3 |
| C | 9.4 | 9.4 | 9.4 |
| D | 15.0 | 13.0 | 11.0 |
| E | - | 1.0 | 1.0 |
| F | 4.2 | 4.2 | 4.2 |
| Properties | | | |
| a_k [kJ/m ²] | 56 | 58 | 59 |
| Vicat B 120 [°C] | 101 | 104 | 110 |
| a_n (weld line) [kJ/m ²] | 15.8 | 17.8 | 17.8 |
| ESC behaviour, failure at ϵ_x [%] | 1.6 | 1.8 | 2.0 |
| UL 94 V 1.6 mm | V-0 | V-0 | V-0 |